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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP94/00852 <b>(22) International Filing Date:</b> 17 March 1994 (17.03.94)  <b>(30) Priority Data:</b> MI93A000553 23 March 1993 (23.03.93) IT  <b>(71) Applicant (for all designated States except US):</b> SOTEN S.R.L. [IT/IT]; Via San Martino, 30/32, I-20017 Rho (IT).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> LANDONI, Guido [IT/IT]; Corso Europa, 197, I-20017 Rho (IT).  <b>(74) Agent:</b> GERVASI, Gemma; Notarbartolo & Gervasi S.r.l., Viale Bianca Maria, 33, I-20122 Milano (IT).		<b>(81) Designated States:</b> AU, BR, CA, CN, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> SINGLE-LAYER BIAXIALLY ORIENTED HEAT-SHRINKABLE FILM COMPRISING LINEAR LOW DENSITY POLY-ETHYLENE AND RELEVANT PRODUCTION PROCEDURE  <b>(57) Abstract</b>  Single-layer biaxially oriented heat-shrinkable film comprising linear low density polyethylene obtained by extrusion and twin-bubble biaxial orientation of a mixture of ethylene/ $\alpha$ -olefin linear copolymer, a polymeric alloy and/or an ethylene-propylene random copolymer and optionally a crystallization inhibitor.		

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SINGLE-LAYER BIAXIALLY ORIENTED HEAT-SHRINKABLE FILM COMPRISING  
LINEAR LOW DENSITY POLYETHYLENE AND RELEVANT PRODUCTION  
PROCEDURE

Prior art

5 The use of linear medium and low density polyethylene for the  
production of single-layer biaxially oriented heat-shrinkable  
film has been known for a long time.

Linear polyethylene has found extensive application in the  
packaging sector as heat-shrinkable films, which require a good  
10 transparency and gloss, high mechanical resistance combined  
with high shrinking values.

Generally, however, there are various reasons for the biaxial  
orientation of linear polyethylene being harder than that  
of normal branched polyethylene.

15 First of all, orientation is hindered by the polymer structure  
being free from long branched chains and having a higher  
crystallinity percentage.

Furthermore, the density being the same, linear polyethylene -  
compared with branched polyethylene - exhibits the following  
20 characteristics:

- a higher melting point by 10°C to 20°C approx.
- just a few very short side chains
- narrow molecular weight distribution.

Collectively, the above features hinder orientation.

25 However, the experimentation on linear polyethylene was a

source for the development of particular types of such polyethylene suitable for orientation.

For example, USP 4,497,920 (Du Pont) claims the production of a heat-shrinkable film consisting of an ethylene/ $\alpha$ -olefin linear  
5 copolymer having two distinct crystalline melting points below 128°C.

The existence of two melting areas according to the above patent allows an easy biaxial orientation of the film, which can be processed between the two melting points.

10 As known, polymers like linear polyethylene which tend to crystallize on cooling generally exhibit one crystalline melting point by calorimetric analysis.

It is, therefore, very hard to determine the temperature or a temperature range at which the extruded tubular film is  
15 sufficiently ductile for blowing (with biaxial orientation) and at the same time sufficiently tough to resist blowing pressure. It follows that the twin-bubble orientation of crystallizable polymers (linear polyethylene, polypropylene and polyolefins in general) is extremely critical, in particular in the case of a  
20 single-layer film.

#### Summary

It has surprisingly been found that a single-layer heat-shrinkable film comprising linear low density polyethylene can be obtained by a procedure comprising the steps of:

25 a) preparing a mixture consisting of:

- an ethylene/ $\alpha$ -olefin linear copolymer,
- a polymeric alloy and/or an ethylene-propylene random copolymer, and optionally
- a crystallization inhibitor;

5 b) extruding, in the melted state, the mixture obtained under a);

c) rapid cooling of the tubular film leaving the extrusion die to a temperature of 28°C to 32°C and subsequent heating to a temperature close to softening;

10 d) biaxially orienting the film by the twin-bubble technique;

e) rapid cooling of the biaxially oriented film to 25°C-35°C.

The claimed procedure allows an easy and precise control of the operating parameters as well as the obtainment of films with improved mechanical, optical and heat seal resistance properties.

15

#### Detailed description of the invention

The present invention contemplates a single-layer biaxially oriented heat-shrinkable film comprising linear low density polyethylene and relevant production procedure.

20 The primary component of said film is an ethylene/ $\alpha$ -olefin linear copolymer with 4-8% by wt.  $\alpha$ -olefin.

Said copolymer is added with 10 to 40% by wt. heterophasic polymers alloy composed of a matrix consisting of propylene homopolymer and a disperse phase consisting of a synthetic elastomer, e.g. ethylene/propylene.

25

The ethylene/ $\alpha$ -olefin linear copolymer may be alternatively or also added with 10 to 50% by wt. ethylene-propylene random copolymer. A non-alternative additive may be an oligomer of the so-called crystallinity inhibitors group.

5 The addition, if any, of said oligomer in a by wt. % amount ranging from 1 to 20 in respect of the basic copolymer depends on the type of primary mixture (more or less rich in crystallizable polymeric components), on the procedure and on the operating conditions (more or less favouring crystals  
10 formation), and to the desired final characteristics of the product.

In particular, the expression "linear ethylene/ $\alpha$ -olefin copolymer" means a copolymer of ethylene and from 4 to 8% by wt. butene or octene or  $\alpha$ -methyl pentene, having linear  
15 molecular chains without branchings and without cross-links. The preferred  $\alpha$ -olefin is octene.

The copolymer density ranges from 0.900 to 0.935 g/cm<sup>3</sup> and melt index from 0.7 to 4.0.

The expression "polymeric alloy" - also known as "catalloy" -  
20 means a product obtained by catalytic reaction composed of a matrix consisting of propylene homopolymer and a disperse phase (copolymer).

In particular, the disperse phase of said alloys may consist of  $\alpha$ -olefins of the C<sub>2</sub>-C<sub>3</sub> or C<sub>3</sub>-C<sub>4</sub> type.

25 Density is 0.88 to 0.90 g/cm<sup>3</sup> and melt index is 0.7 to 4.

The expression "ethylene-propylene random copolymer" means a synthetic product obtained from ethylene and propylene, the latter being the major component, e.g. 10% ethylene and 90% propylene.

5 Out of the oligomers inhibiting crystallization, the following products are suitable for the purpose:

aliphatic and aromatic hydrocarbon resins, aliphatic and aromatic copolymers, such as piperylene, methylbutene, vinyltoluene, indene,  $\alpha$ -methylstyrene, polycyclodiene, etc.,  
10 hydrogenated C<sub>9</sub> resins, styrene,  $\alpha$ -methylstyrene, isobutene, pinene and rosin resins, and terpene resins.

The ethylene/ $\alpha$ -olefin linear copolymer can be hardly oriented by the twin-bubble procedure.

In fact, on approaching the crystalline melting point, the  
15 polymer loses consistency and the bubble obtained by tubular film inflation is extremely unstable.

We have found that the addition of ethylene-propylene polymeric alloy and/or of ethylene-propylene random copolymer yields a mixture that can be easily handled thanks to its wide  
20 temperature range within which the tubular film is sufficiently ductile to be blown and sufficiently tough to resist blowing pressure.

A further possibility of mixture adjustment consists in the addition of crystallization inhibitory oligomers.

25 The present invention introduces some innovations in the

traditional twin-bubble procedure, which allow an accurate product control during the process critical phases.

According to the claimed procedure, proper proportions of the single components are mixed in a conventional slow mixer with  
5 separate mixture preparation or by an automatic mixing and metering apparatus on the extruder hopper.

Extrusion is carried out by single-screw extruders, 28-32 diameters long.

The melted mixture leaves the extruder die in a tubular form at  
10 a temperature of 180°C to 205°C. The tubular film diameter is a function of the desired max. stretching ratio of the final film.

As concerns polyolefins, it is usual practice to use a balanced stretching ratio in the two directions (longitudinal and  
15 transversal), which ratio may range from 4 to 6. The stretching ratio used in the claimed procedure is 1:4.5 approx.

The tubular film leaving the extruder is sized and cooled by a new method in respect of the conventional twin-bubble extrusion technique. In particular, the tubular film, which is still hot,  
20 is sized by passing between an outer ring, wherefrom a liquid coolant at 15°C-25°C flows continuously, and a mould, internal to the tubular film, which is also cooled by a liquid coolant at 15°C-25°C.

The max. temperature variation along the tubular film  
25 circumference is 1°C. A more uniform thickness and a greater



homogeneity of the extruded material are thus secured.

By internal and external cooling the tubular film temperature drops to 28°-32°C in few seconds, preferably within 4 to 9 sec.

The water leaving the outer ring adheres, as a liquid film, to  
5 the tubular film outer surface and flows to the chamber underneath.

This provides an accurate control of the rate of crystal formation in the product.

The cold tubular film is then fed to an IR-ray or hot-air oven  
10 where it is heated to a temperature close to softening. Once heated to the desired temperature, the tubular film is inflated with compressed air and expanded in the transversal direction.

This results in a transversal orientation of the molecules.

The tubular film inflation is carried out by controlling the  
15 operating temperature within  $\pm 1^\circ\text{C}$ .

At the same time, the tubular film is stretched in the longitudinal direction by causing the pull-roll upstream of the oven and the final pull-roll to operate at a different speed.

20 Once the film has undergone double hot stretching, it is rapidly cooled to maintain the inner orientation of molecules, resulting from transversal inflation and longitudinal stretching.

To this purpose, the stretched film is cooled to 25°C-35°C by  
25 blowing air at 5°C to 15°C within 15 to 30 sec.

The film obtained according to the claimed procedure is 10 to 40  $\mu\text{m}$  thick and exhibits improved characteristics over the product obtained by the known technique.

In particular, the film of the invention having thickness  
5 between 12 and 25  $\mu\text{m}$  exhibits:

- haze: from 1.0 to 2.0% depending on thickness
- surface gloss at 20°C: from 100 to 120 units
- tensile strength: from 100 to 120 N/mm<sup>2</sup>
- shrinking at 120°C: from 50 to 60%, balanced in the two  
10 directions
- heat seal resistance: >60 N/mm<sup>2</sup>
- tearing propagation: from 10 to 25 g depending on thickness.

Furthermore, the procedure under the invention gives a film with characteristics tailored to the various uses.

15 Thanks to the above characteristics, the film as per the present invention is suitable for the packaging sector in general and in particular for the applications requiring a good film shrinkage and adhesion to the packed product as well as a good mechanical and heat seal resistance. For example, the  
20 claimed film is particularly fit for the packaging of vegetables, boxes, food also of irregular shape, books and magazines, multiple packed products, etc.

The following examples are conveyed by way of illustration, not of limitation.

## EXAMPLE 1

A single-layer film, 15  $\mu\text{m}$  thick, consisting of the following raw materials was produced.

The basic polymer used was linear polyethylene containing 8 %  
5 by wt. octene (melt index 1 and sp. gr. 0.923), in particular Clear Flex FG 308 produced by Enichem Polimeri.

Said polymer was added with 20% by wt. propylene-ethylene polymeric alloy (melt index 0.8 and density  $0.89 \text{ g/cm}^3$ ), in particular the elastomeric copolymer Hi Fax 7023 XEP produced  
10 by HIMONT.

The crystallinity inhibitor was a completely saturated hydrogenated hydrocarbon resin, Eastotac 140 produced by Eastman Kodak, having molecular weight of 900 approx. and Brookfield viscosity of 1000 approx. Said resin, after  
15 dispersion in low density polyethylene (50%) to give the masterbatch (Prisma AD WAX 90237 produced by Frilvam) was added to the basic polymer mixture in a 5% amount equivalent to 2.5% pure resin.

Finally, antiblock and sliding additives were used to improve  
20 film handling in production and application phases. In particular, 0.5% micronized silicon dioxide was used as antiblock agent (equivalent to 1% masterbatch of type AB 6004 produced by Constab).

The operating conditions were as follows:

25 - temperature of the melted material leaving the die:  $181^\circ\text{C}$

- cooling water:  $19^{\circ}\text{C} \pm 1$
- cooling temperature of tubular film leaving the die:  $30^{\circ}\text{C}$
- cooling time of tubular film leaving the die: 5 sec
- diameter of tubular film leaving the die: 180 mm
- 5 - longitudinal/transversal stretching ratio: 4.5
- tubular film blowing temperature:  $120^{\circ}\text{C}$
- cooling temperature of stretched tubular film:  $30^{\circ}\text{C}$
- cooling time of stretched tubular film: 20 sec.

Table 1 shows the characteristics of the film obtained and, for  
10 the purpose of comparison, the characteristics of commercial  
product CLYSAR LLP (DuPont).

The film obtained according to Example 1 showed an improved  
tear strength in respect of CLYSAR LLP.

#### EXAMPLE 2

15 The procedure of Example 1 was repeated with the difference  
that the mixture of raw materials was further added with  
ethylene-propylene random copolymer (melt index 1.8), in  
particular with 10% Moplen EP2 S 34 F (HIMONT).

The type and quantity of hydrocarbon resin and of antiblock and  
20 sliding additives remained unchanged.

The product obtained showed higher elastic modulus and improved  
optical characteristics. It was also stiffer than that as per  
Example 1 and, therefore, more adequate for use in automatic  
fast packaging machines.

25 Also handling conditions improved, the bubble stability being

higher.

The melted material temperature ranged from 185°C to 188°C and the tubular film blowing temperature was 126°C.

Table 1 shows the characteristics of the film obtained.

5 Compared with the product as per Example 1, the film had a higher heat seal resistance and improved optical properties.

### EXAMPLE 3

The procedure of Example 1 was repeated with the difference that the mixture was further added with ethylene-propylene  
10 random copolymer (melt index 4), in particular with 10% Moplen SYL 7008 XCP (HIMONT).

The type and quantity of hydrocarbon resin and of antiblock and sliding additives remained unchanged.

The product obtained exhibited improved heat sealing  
15 characteristics (lower sealing temperature in respect of the product as per Example 2, which means shorter sealing times and wider sealing range). Also seal resistance was improved.

Furthermore, like in Example 2, the temperature range was wider than in Example 1, and bubble stability was the same.

20 Operating parameters:

melted product temperature: 185°C

tubular film blowing temperature: 124°C

Table 1 shows the characteristics of the film obtained.

Compared with the products as per the above mentioned Examples,  
25 heat-sealed film had a high tear strength.

## EXAMPLE 4

The procedure of Example 1 was repeated with the difference that the polymeric alloy was completely removed and the quantity of ethylene-propylene random copolymer (melt index 4),  
5 in particular Moplen SYL 7008 XCP (HIMONT) was increased (25%).

The type and quantity of hydrocarbon resin and of antiblock and sliding additives remained unchanged.

The product obtained had excellent heat seal characteristics.

10 On handling, bubble stability and thickness distribution were excellent.

Operating parameters:

melted product temperature: 182°C

bubble blowing temperature: 122°C

15 Table 1 shows the characteristics of the film obtained.

The mechanical properties were worse than in the previous cases.

## EXAMPLE 5

The procedure of Example 1 was repeated with the difference  
20 that the hydrocarbon resin was added in a 1.5% amount in respect of the basic copolymer.

The type and quantity of antiblock and sliding additives remained unchanged.

The product obtained was a medium-stiff and medium-shrinkable  
25 film.

The operating conditions were similar to those of Example 1:

temperature of melted product leaving the die: 183°C

tubular film blowing temperature: 123°C

Table 1 shows the characteristics of the film obtained.

- 5 Compared with the previous products, this film exhibited good mechanical properties and excellent tear strength.

#### EXAMPLE 6

- The procedure of Example 1 was repeated with the difference that the basic copolymer was linear polyethylene (melt index  
10 1.1; sp. gr. 0.920) containing 8% octene, with more uniform distribution (Dowlex NG 5056 E produced by Dow Chemical).

The operating conditions were analogous to those of Example 1 (additional 5°C on extrusion).

- The film characteristics were very similar to those of Clysar  
15 LLP, as shown in Table 1.

#### EXAMPLE 7 (Comparison)

- The procedure of Example 2 was repeated with the difference that the basic resin was added with 7% propylene-ethylene polymeric alloy and with 2% random copolymer.

- 20 All mechanical properties were worse (Table 1).

#### EXAMPLE 8 (Comparison)

The procedure of Example 1 was repeated without addition of polymeric alloy.

- The bubble could not be maintained at stable and uniform  
25 conditions and frequent bursts occurred. No improvement even by

considerably varying all operating conditions. Significant and measurable samples could not be obtained.



TABLE 1: Film characteristics

	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	Commercial CLYSAR LLP (Du Pont)
Thickness $\mu$	15	15	15	15	15	15	15	15
Tensile strength $N/mm^2$	120	130	110	95	125	100	85	100
Elongation at break %	125	115	130	125	130	130	90	130
Heat seal resistance $g/cm$	950	1100	1200	1000	1050	1100	800	1100
Tear strength $g$	20	15	22	18	24	16	10	10
Shrinking at 120°C %	56	55	55	55	53	52	52	50
Haze %	1.7	1.4	1.4	1.2	1.4	1	1.3	1
Gloss (photoelectric cell units)	100	105	105	105	100	110	100	110
Elastic modulus $N/mm^2$	348	360	340	300	352	315	350	300

## CLAIMS

- 1 1. Procedure for the preparation of a single-layer biaxially  
2 oriented heat-shrinkable film comprising linear low density  
3 polyethylene comprising the steps of:
  - 4 a) preparing a mixture consisting of:
    - 5 - an ethylene/ $\alpha$ -olefin linear copolymer,
    - 6 - a polymeric alloy and/or an ethylene-propylene random  
7 copolymer, and optionally
    - 8 - a crystallization inhibitor;
  - 9 b) extruding, in the melted state, the mixture obtained under  
10 a);
  - 11 c) rapid cooling of the tubular film leaving the extrusion die  
12 to 28°C to 32°C and subsequent heating to a temperature close  
13 to softening;
  - 14 d) biaxially orienting the film by the twin-bubble technique;
  - 15 e) rapid cooling of the bioriented film to 25°C-35°C.
- 1 2. The procedure according to claim 1 wherein said ethylene/ $\alpha$ -  
2 olefin linear copolymer contains from 4 to 8% by wt.  $\alpha$ -olefin  
3 selected out of the group consisting of butene, octene, hexene,  
4 and  $\alpha$ -methylpentene.
- 1 3. The procedure according to claim 1 wherein said ethylene/ $\alpha$ -  
2 olefin linear copolymer has density ranging from 0.900 to 0.935  
3 g/cm<sup>3</sup> and melt index ranging from 0.7 to 4.0.
- 1 4. The procedure according to claim 1 wherein said polymeric

2 alloy is a product obtained by catalytic reaction, composed of  
3 a matrix consisting of a propylene homopolymer and a disperse  
4 phase consisting of C<sub>2</sub>-C<sub>3</sub>  $\alpha$ -olefins.

1 5. The procedure according to claim 1 wherein said ethylene-  
2 propylene random copolymer is obtained by the synthesis of  
3 ethylene and propylene, the latter being the major component.

1 6. The procedure according to claim 1 wherein said  
2 crystallization inhibitor is selected out of the group  
3 consisting of aliphatic and aromatic hydrocarbon resins,  
4 piperylene, methylbutene, vinyltoluene, indene,  
5  $\alpha$ -methylstyrene, styrene, pinene and rosin resins, and terpene  
6 resins.

1 7. The procedure according to claim 1 wherein said mixture  
2 prepared under step a) contains 10 to 40% by wt. of said  
3 polymeric alloy in respect of said ethylene/ $\alpha$ -olefin linear  
4 copolymer and/or 10 to 50% of said ethylene-propylene random  
5 copolymer and, if necessary, 1 to 20% of said crystallization  
6 inhibitor.

1 8. The procedure according to claim 1 wherein said cooling of  
2 step c) causes the tubular film temperature to drop to 28°C to  
3 32°C in 4-9 seconds.

1 9. The procedure according to claim 1 wherein said biaxial  
2 orientation is obtained at a longitudinal/transversal  
3 stretching ratio of 1:4.5.

1 10. The procedure according to claim 1 wherein said cooling of

2 step e) causes the tubular film temperature to drop to 25°C to  
3 35°C in 15-30 seconds.

1 11. Single-layer biaxially oriented heat-shrinkable film  
2 made of composition comprising:

- 3 - a linear low density polyethylene,  
4 - an ethylene/ $\alpha$ -olefin linear copolymer with 4-8% by wt.  
5  $\alpha$ -olefin,  
6 - a polymeric alloy and/or an ethylene-propylene random  
7 copolymer, and optionally  
8 - a crystallization inhibitor.

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International Application No

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## A. CLASSIFICATION OF SUBJECT MATTER

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Y	EP,A,0 423 387 (HEISEI POLYMER CO.,LTD) 24 April 1991 *whole document* ---	1-11
A	EP,A,0 519 837 (ECP-ENICHEM POLYMERES FRANCE S.A.) 23 December 1992 see claims ---	1-11
A	EP,A,0 321 220 (MITSUI PETROCHEMICAL INDUSTRIES, LTD) 21 June 1989 see page 2, line 50 - page 3, line 17; claims --- -/--	1-11



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Int: onal Application No

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